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EXAMINATION OF SHALE-DERIVED POLAR COMPOUNDS AND  
THEIR EFFECTS ON DIESEL FUEL STABILITY

By

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INTRODUCTION

Polar heterocyclic compounds present in middle distillate fuels have been implicated in the chemical processes involved in fuel instability. Nitrogen-containing aromatics (e.g., pyrroles, pyridines, quinolines, indoles) are often intimately involved in the reactions leading to deposition of insoluble sediments and gums in both petroleum and shale-derived fuels (1, 2). Although results of fuel dopant studies are useful in screening potentially active compounds, the results must be taken with caution (3, 4). For example, the particular accelerated (i.e., high temperature) stress regimen employed may have a variable effect upon the results obtained. Additionally, interactive effects between labile species need to be assessed in greater detail (2, 4).

One of the approaches we have used in the study of diesel fuel storage stability has been to examine the effects of adding shale-derived polar fractions to a stable shale base fuel. Thus, we have isolated polar compounds from two different shale sources by mild acid extraction followed by adsorption on silica gel. The identification of the extract components by combined gas chromatography - mass spectrometry, as well as the results of accelerated storage stability tests, are described in this paper.

EXPERIMENTAL

Storage Test Techniques

The accelerated storage stability test method used has been described in detail (3). In summary, 300 ml samples of filtered fuel were stressed in the dark in 500 ml screw-cap borosilicate Erlenmeyer flasks (Teflon-lined caps). All samples were run in duplicate and appropriate blank flask/filter holder corrections were applied. Both filterable sediment and adherent gum values were determined after stress.

Hydroperoxide levels were determined in samples of filtered, stressed fuel by iodometric titration (ASTM D1583-60).

Instrumental Methods

The nitrogen compound extracts were examined by combined GC/MS (EI mode). The GC/MS unit consisted of a Hewlett-Packard Model 5710 GC, a H-P Model 5982A mass spectrometer and a Ribermag SADR GC/MS data system. An all-glass GC inlet system was used in conjunction with a 0.31 mm x 50 m SP2100 (similar to OV-101) fused silica capillary column (5). Operational parameters included: sample size - 2 to 3 microliters split at 60:1, column flow - 1.1 to 1.2 ml/min at a head pressure of 10.5 PSI, detector gain - 9 X LOW, injection port - 250°C, temperature program - 70°C (2 min hold), 4°C/min programmed temperature rise, 220°C (16 min final hold).

Nitrogen concentration levels in fuel samples were determined with an Antek Model 720 nitrogen analyzer using a Dohrmann Model S-300 combustion furnace operating at 1000°C. Three-microliter samples were analyzed in quadruplicate (at the minimum) with the actual nitrogen concentration calculated by comparison with nitrogen calibration standards.

Base Fuel

The base fuel for the present study was diesel fuel marine (DFM) refined from Paraho crude shale oil by SOHIO. This fuel was produced in the U.S. Navy's Shale-II demonstration and is well-characterized (2). A quantity of this fuel was available which contained no additives (sample "D-1"). The D-1 fuel contained 15 ppm N (w./v.) and exhibited good storage stability (2).

Nitrogen Compound Source Fuels

Two high-nitrogen middle distillate fuels produced in U. S. Navy shale programs were selected for extraction studies. Sample "Shale-I DFM" was produced by a delayed coking process

followed by fractionation and was finished by extraction with high strength sulfuric acid (6-8). Sample "Shale-II DFM Composite" was produced by moderate hydrotreatment of the total crude followed by fractionation. This sample was a composite of several streams from the refining run prior to acid extraction. A final extraction with 92% sulfuric acid was used to produce the finished Shale-II DFM (which is the same as sample D-1, the base fuel in the present study) (9, 10).

#### Extraction Procedure

As shown in Figure 1, the Shale-I DFM and Shale-II DFM Composite fuels were initially subjected to extraction with a 25% molar excess of 0.20 N HCl. The quantity of acid used was calculated by assuming that all of the nitrogen present in the fuel was basic or extractable. The extraction process was conducted for both fuels on a 10 liter scale. The single acid extractions were accomplished with 2 liters of fuel in a 4 liter separatory funnel. A portion of the fuel to be extracted was placed in the funnel with the appropriate quantity of 0.20 N HCl. The contents were vigorously swirled for 5 min, allowed to stand 5 min, gently swirled for 5 min (to reduce the number of emulsion particles) and allowed to stand for 10 min. After careful separation of the layers, traces of acid were removed from the fuel sample by washing with water. The "basic" nitrogen compounds (BNC extracts) were isolated by neutralizing the combined aqueous acid extracts to pH 8-9 ( $\text{NaHCO}_3$ ), extracting the mixture twice with methylene chloride, drying the combined organic layer ( $\text{anh. MgSO}_4$ ) and removing the solvent gently by rotary evaporation (verified by GC).

The residual polar material (including non-basic nitrogen compounds, the "NBNC" extracts) was removed from both acid-extracted fuels by batch silica gel adsorption. Again, it was decided to employ a relatively mild separation technique to avoid extensive chemical alteration of the polar species present. Thus, 2 liters of fuel were treated once with 400 g of fully activated Grade 923 silica gel (100-200 mesh, W. R. Grace) with stirring for a 3h period. Gravity filtration afforded ca. 1550 ml of silica-extracted fuel (filtrate) and a quantity of moist silica. Excess fuel was desorbed from the moist silica by several washings with pentane (ca. 2.5 liters). The silica was next equilibrated several times with methylene chloride (8 x 500 ml). The methylene chloride NBNC extracts were combined and retained. Following this treatment, the silica gel was treated with methanol (1 x 1 liter), filtered and the methanol wash was retained (methanolic NBNC extract).

## RESULTS AND DISCUSSION

Preliminary accelerated storage stability tests at 43°C and 80°C indicated that both Shale-I DFM and Shale-II DFM Composite were relatively unstable (i.e., much greater than 1.0 mg/100 ml of total insolubles at 14 days - 80°C) middle distillate fuels. Although both fuels were "unstable", the Shale-I DFM was by far the less stable. Both fuels were found to be relatively high in nitrogen content (Table I). Thus, it was considered that the differences in stability of the fuels might result from the presence of different nitrogen compound types and/or interactive effects. The high nitrogen contents of the fuels made them convenient sources of extractable material for the doping experiments which followed.

TABLE I

#### STORAGE STABILITY OF NITROGEN COMPOUND SOURCE FUELS

Fuel	N Conc. (ppm-w/v)	Conditions	Total Insolubles (mg/100 ml)	Std. Dev. <sup>a</sup>
Shale-I DFM	1955	43°C/49d	58.6	30.0 (4)
		43°C/92d	113.6	59.5 (4)
		80°C/4d	52.2	8.2 (4)
		80°C/7d	76.8	24.4 (4)
		80°C/14d	138.9	57.5 (8)
Shale-II DFM Composite	3505	80°C/14d	20.5	0.8 (2)

a. Number of trials indicated in parentheses.

#### Extraction of Nitrogen Compounds

The separation scheme which was employed for the removal of polar, nitrogen-rich extracts from both source fuels is summarized in Figure 1. A single, mild acid extraction was selected (0.20 N HCl) so that the opportunity for chemical changes in the fuel would be minimized (e.g., alkyldpyrroles are known to be acid-sensitive (11)). The BNC extracts from both fuels were

obtained in methylene chloride solution. Subsequent treatment of the acid-extracted fuels with silica gel afforded two NBNC extracts for each fuel (methylene chloride and methanol).

Samples of Shale-I DFM and Shale-II DFM Composite were analyzed for soluble nitrogen content following treatment with acid and silica gel. The nitrogen balance data, which appear in Table II, indicate that well over 90% of the nitrogen originally present in the fuels was accounted for. The final entries (line 8) in the table may be explained by nitrogen compounds still adsorbed to the silica and/or analytical imprecision. Although several trial extractions (on a 10 ml scale) were able to remove the bulk of the nitrogen present in Shale-I DFM, the actual batch extraction processes were seen to be far less efficient. Thus, although 55% of the nitrogen in the Shale-II DFM Composite was acid extractable, only about 10% of the nitrogen in the Shale-I DFM was acid extractable under these conditions. Line 3 in Table II refers to data obtained immediately prior to treatment of the fuels with silica gel. Since there had been approximately a four month interval between the acid and silica gel treatments, it was necessary to refilter the fuels and redetermine soluble nitrogen levels.

TABLE II

NITROGEN ANALYSES FOR EXTRACTED NITROGEN COMPOUND SOURCE FUELS

Sample	N Concentration (ppm-w/v)	
	Shale-I DFM	Shale-II DFM Composite
1. Original	1955	3505
2. After acid extraction	1757	1570
3. Before silica treatment	1720	1560
4. Isolated in $\text{CH}_2\text{Cl}_2$ wash of silica	246	685
5. Isolated in $\text{CH}_3\text{OH}$ wash of silica	139	380
6. After acid and silica treatment	1286	370
7. Sum of 4-6	1671	1435
8. Deficit in N balance <sup>a</sup>	(49)	(125)

a. The difference of lines 3 and 7.

The accelerated storage stabilities of the extracted source fuels were examined (Table III). The results of duplicate trials indicated that the fuels remained relatively unstable despite the treatment with acid and silica. It is noteworthy that the mild acid treatment may have actually deteriorated the stability of both fuels by a small degree. In addition, Shale-II DFM Composite remained a fairly unstable fuel despite the removal of 89% of its original nitrogen content by the extractions.

TABLE III

STORAGE STABILITY OF EXTRACTED NITROGEN COMPOUND SOURCE FUELS  
(14 day/80°C Stress)

Fuel	Sample	N Conc. (ppm-w/v)	Total Insolubles (mg/100 ml)	Std. Dev.
Shale-I DFM	Original	1955	138.9	57.5
	Acid extracted	1757	152.6	9.8
	Acid and silica extracted	1286	179.4	103.2
Shale-II DFM Composite	Original	3505	20.5	0.8
	Acid extracted	1570	33.8	0.2
	Acid and silica extracted	370	16.4	1.0

Examination of Nitrogen Compound Extracts

Compounds present in the BNC, NBNC ( $\text{CH}_2\text{Cl}_2$ ) and NBNC ( $\text{CH}_3\text{OH}$ ) extracts from both source fuels were examined by GC/MS. The conditions used permitted excellent separation of the compounds present. Both total and selected ion-counting techniques were employed, with peaks being identified on the basis of fragmentation pattern and Z-series (5). Frequently, two or more compounds would be present in a peak, so that the relative amount of each was approximated by the magnitude of the total ion count for a given fragmentation pattern. Peak areas were determined by integration of the total ion count over the entire peak.

The results for the acid extract components (BNC) from Shale-I DFM are summarized in Table IV. Sixty-eight well-resolved major peaks were analyzed and over 180 distinct nitrogen compounds were identified by class and carbon number. Substituted pyridines represented by far the largest class of compounds present, comprising about 87% of the material identified. Also present were quinolines and tetrahydroquinolines. Other nitrogen compounds comprised the remainder of the materials examined. The peaks which were examined represent at least 75% of the total sample peak area and are, thus, representative of the total sample.

TABLE IV  
EXAMINATION OF BNC EXTRACT FROM SHALE-I DFM

<u>Compound Class<sup>a</sup></u>	<u>No. Isomers</u>	<u>Area %</u>
A. Pyridines	<u>(81)</u>	<u>(87.1)</u>
C <sub>7</sub>	2	1.5
C <sub>8</sub>	10	9.6
C <sub>9</sub>	24	24.5
C <sub>10</sub>	22	22.2
C <sub>11</sub>	15	17.6
C <sub>12</sub>	8	11.8
B. Quinolines	<u>(53)</u>	<u>(7.0)</u>
C <sub>2</sub>	1	<0.1
C <sub>3</sub>	3	0.6
C <sub>4</sub>	10	1.2
C <sub>5</sub>	17	2.7
C <sub>6</sub>	18	2.1
C <sub>7</sub>	4	0.3
C. Tetrahydroquinolines	<u>(40)</u>	<u>(4.1)</u>
C <sub>1</sub>	1	<0.1
C <sub>2</sub>	1	0.1
C <sub>4</sub>	9	0.9
C <sub>5</sub>	7	0.6
C <sub>6</sub>	10	1.0
C <sub>7</sub>	8	0.7
C <sub>8</sub>	4	0.8
D. Indoles	<u>(5)</u>	<u>(0.4)</u>
E. Others <sup>b</sup>	<u>(4)</u>	<u>(1.4)</u>

a. C<sub>x</sub> listing under each class denotes the number of carbon atoms in substituents on the heterocyclic ring.

b. Triazines, alkylamines.

Results for the BNC extract of Shale-II DFM Composite appear in Table V. Again, alkylpyridines were the principal components (ca. 77% of the identified material) with a good amount of

tetrahydroquinolines present as well (18.5%). The larger amount of tetrahydroquinolines in the Shale-II DFM Composite (relative to the Shale-I DFM) is a reflection of the hydrotreatment which this fuel was subjected to during its processing.

TABLE V  
EXAMINATION OF BNC EXTRACT FROM SHALE-II DFM COMPOSITE

Compound Class <sup>a</sup>	No. Isomers	Area %
A. Pyridines	<u>(48)</u>	<u>(77.5)</u>
C <sub>3</sub>	2	2.0
C <sub>4</sub>	2	2.6
C <sub>5</sub>	3	2.8
C <sub>6</sub>	7	5.6
C <sub>7</sub>	7	9.6
C <sub>8</sub>	9	24.3
C <sub>9</sub>	12	20.7
C <sub>10</sub>	5	8.9
C <sub>11</sub>	1	1.1
B. Tetrahydroquinolines	<u>(40)</u>	<u>(18.5)</u>
C <sub>0</sub>	2	0.2
C <sub>1</sub>	2	0.5
C <sub>2</sub>	3	1.0
C <sub>3</sub>	9	5.6
C <sub>4</sub>	14	9.5
C <sub>5</sub>	9	1.8
C <sub>6</sub>	1	0.1
C. Quinolines	<u>(15)</u>	<u>(2.2)</u>
C <sub>1</sub>	1	<0.1
C <sub>2</sub>	1	0.2
C <sub>3</sub>	5	1.2
C <sub>4</sub>	7	0.7
C <sub>5</sub>	1	<0.1
D. Indoles	<u>(9)</u>	<u>(1.3)</u>
E. Indolines	<u>(2)</u>	<u>(0.5)</u>

a. C<sub>x</sub> listing under each class denotes the number of carbon atoms in substituents on the heterocyclic ring.

Table VI indicates the identifications of the ten largest peaks present in the BNC extracts from both fuels. As can be seen, tri- and tetra-alkylpyridines were prevalent in both extracts.

Two components (denoted by asterisks) appeared to be common to both fuels. The ten largest peaks correspond to approximately 32% of the total identified area for the Shale-I DFM and 45% for the Shale-II DFM Composite.

TABLE VI

A. TEN LARGEST PEAKS - BNC EXTRACT FROM SHALE-I DFM

Rank	Rel. Area	Main Component	Retention Time (min.)
1	1000	Dimethylheptylpyridine	30:49*
2	754	Dimethylnonylpyridine	37:50
3	740	Dimethylheptylpyridine	36:59
4	663	Trimethylheptylpyridine	32:53*
5	659	Dimethyloctylpyridine	34:49
6	630	Dimethylheptylpyridine	31:40
7	607	Dimethyloctylpyridine	33:57
8	586	a C <sub>12</sub> Pyridine	38:35
9	537	Trimethyloctylpyridine	35:57
10	513	Trimethylhexylpyridine	36:30

B. TEN LARGEST PEAKS - BNC EXTRACT FROM SHALE-II DFM COMPOSITE

Rank	Rel. Area	Main Component	Retention Time (min.)
1	1000	Dimethylheptylpyridine	30:47*
2	908	Dimethylhexylpyridine	27:32
3	682	Trimethylpentylpyridine	26:31
4	662	Dimethylhexylpyridine	28:25
5	639	Dimethylpentylpyridine	24:06
6	635	Methylpropyltetrahydroquinoline	26:42
7	508	Dimethylpentylpyridine	27:24
8	450	Trimethylpentylpyridine	30:19
9	432	Trimethylheptylpyridine	32:53*
10	427	Trimethylhexylpyridine	29:46

\* These two components are common to both BNC extracts.

Both NBNC extracts (i. e.,  $\text{CH}_2\text{Cl}_2$  and  $\text{CH}_3\text{OH}$  solubles from silica gel treatment) for both source fuels were found to be exceedingly complex. The methylene chloride NBNC extract for Shale-I DFM consisted primarily of alkylbenzenes, indenenes, tetralins, naphthalenes and other hydrocarbons. A good variety of substituted indoles was present together with lesser amounts of pyridines, tetrahydroquinolines and quinolines. Trace quantities of alkylpyrroles were detected. The methanolic NBNC extract for this fuel was for the most part a mixture of straight-chain carboxylic acids and alkylpyridines. Small amounts of alcohols, indoles, amines, quinolines and pyrroles were detected.

The methylene chloride NBNC extract for Shale-II DFM Composite consisted largely of alkylbenzenes, indenenes, naphthalenes and hydrocarbons. A good variety of oxygen-containing species was found (esters and ketones). Most of the nitrogen in this extract appeared in the form of substituted indoles. Lesser amounts of carbazoles and pyridines were detected; no alkylpyrroles were found. The methanolic NBNC extract was found to be rich in alkylpyridines with trace levels of indoles detected. Once again, alkylpyrroles did not appear to be present. The presence of pyridines in the methanolic NBNC extracts from both source fuels is indicative of the inefficiency of the mild, batch acid extraction employed. Adsorption chromatography techniques have recently been applied to samples of Shale-I DFM (12) and Shale-II DFM Composite (13) in efforts to achieve analytical separations. Results obtained by these workers are consistent with the GC/MS and nitrogen concentration analyses reported in this paper.

#### Results of Doping Experiments

Nitrogen compound extracts (BNC, NBNC ( $\text{CH}_2\text{Cl}_2$ ), NBNC ( $\text{CH}_3\text{OH}$ )) from both source fuels were added as dopants to a stable shale DFM base, fuel D-1. The extracts which were added were solvent-free (verified by GC) and were immediately taken up in the appropriate quantity of D-1 following solvent-stripping. Nitrogen concentrations in the doped D-1 were then determined, with the amount of added nitrogen being calculated by subtracting the 15 ppm N (w/v) present in the

undoped base fuel. Stress conditions employed temperatures of 80°C and 43°C for periods of time ranging up to 14 and 96 days, respectively (3).

The results of doping experiments with the BNC extracts are shown in Table VII. The amount of total insoluble material reported is the mean of three experimental trials. On a ppm N basis, the BNC extract derived from Shale-I DFM was the more potent sediment promoter; however, relatively low levels of insoluble material were generally observed in all trials. Hydroperoxide levels were also determined in the filtrates of stressed samples. Samples of D-1 which had been doped with BNC from Shale-I DFM showed the highest peroxide numbers.

TABLE VII  
STORAGE STABILITY OF D-1 WITH ADDED BNC EXTRACTS

BNC Source	Stress Conditions	N Added (ppm-w/v)	Total Insolubles (mg/100 ml)	Peroxide Number <sup>a</sup> (meq ROOH/kg fuel)
Shale-I DFM	43°C/49d	72	1.2	106.8 (2.2)
	43°C/92d	72	1.2	180.0 (8.1)
	80°C/7d	72	2.2	40.1 (8.1)
	80°C/14d	72	5.9	52.8 (52.5)
Shale-II DFM Composite	43°C/49d	545	3.4	15.5 (9.5)
	43°C/96d	545	4.8	25.1 (15.4)
	80°C/7d	545	2.5	22.0 (19.1)
	80°C/14d	545	4.2	13.1 (52.5)

a. Fuel blank values (i. e., undoped D-1) in parentheses.

In a similar manner, accelerated storage stability tests were conducted with the NBNC extracts from both sources in fuel D-1. The results, summarized in Table VIII, indicate that the methanolic NBNC extracts were active sediment promoters in D-1. On a ppm N (w/v) basis, the Shale-I DFM NBNC (CH<sub>3</sub>OH) extract was 58% as effective as 2,5-dimethylpyrrole in promoting the formation of insoluble material (3). Since this extract was rich in alkylpyridines and carboxylic acids, it is possible that interactive effects between active species defined the efficacy of the dopant as an agent of fuel instability. All NBNC extract trials indicated that those extracts derived from Shale-I DFM were more active in promoting sediment.

TABLE VIII  
STORAGE STABILITY OF D-1 WITH ADDED NBNC EXTRACTS

NBNC Source	Extraction Solvent	Stress Conditions	N Added (ppm-w/v)	Total Insolubles (mg/100 ml)
Shale-I DFM	CH <sub>2</sub> Cl <sub>2</sub>	43°C/49d	120	6.2
		43°C/91d	120	6.7
		80°C/7d	120	8.7
		80°C/14d	120	12.2
		80°C/14d	155	35.1
	CH <sub>3</sub> OH	80°C/14d	155	35.1
Shale-II DFM Composite	CH <sub>2</sub> Cl <sub>2</sub>	43°C/49d	370	1.5
		43°C/91d	370	1.4
		80°C/7d	370	0.9
		80°C/14d	370	1.2
		80°C/14d	398	16.9
	CH <sub>3</sub> OH	80°C/14d	398	16.9

#### CONCLUSIONS

Nitrogen-rich polar fractions have been isolated and characterized from two unstable shale diesel liquids. When these extracts were doped into a stable shale DFM and stressed at elevated temperatures, the formation of insoluble material was observed. The activity of a given polar extract in the promotion of instability behavior in a stable base fuel was a complex function of interactive effects between active species in the fuel.

# NITROGEN COMPOUND EXTRACTION SCHEME

NITROGEN COMPOUND  
SOURCE FUEL

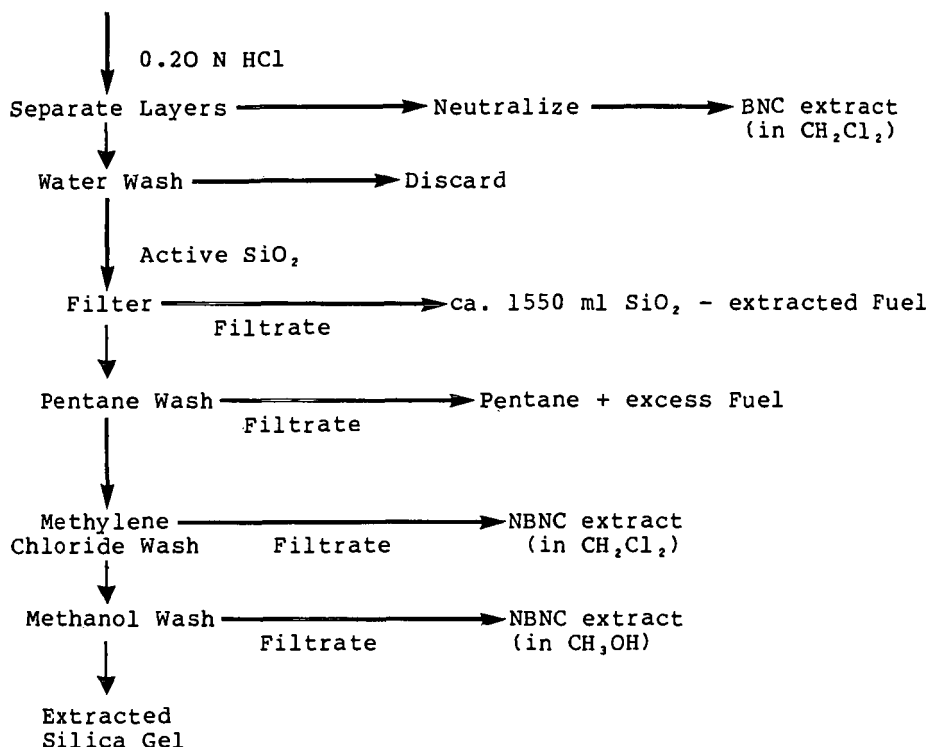


Figure 1



#### ACKNOWLEDGMENT

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